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On the chemical grafting of titanium nitride by diazonium chemistry†

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Current research directions with the aim of extending the applications of titanium nitride (TiN) in areas of microelectronics, electrocatalysis, biosensors *etc.* require identifying new and efficient methods to modify this durable material with desired organic functionalities. We have clearly demonstrated in this work that diazonium chemistry can be considered for surface modification of titanium nitride. Indeed, a near-monolayer of aminophenylene has been reported to be spontaneously grafted onto the TiN surface by simple immersion of the substrates into an acidic solution of the corresponding diazonium cations. X-ray photoelectron spectroscopy measurements strongly suggested a covalent coating of aminophenyl groups on titanium nitride. Surface functionalization with aminophenylene layers was also investigated in presence of hypophosphorous acid and iron powder. Effect of these homogeneous and heterogeneous reducing agents with respect to the formation of aryl layers at different thicknesses was discussed in detail on the basis of conventional hemolytic dediazoniation mechanism in combination with the XPS results.

Introduction

Titanium nitride compounds are unique ceramic materials exhibiting both metallic (Ti–Ti) and covalent (Ti–N) bonding characteristics. Electrical conductivity and metallic reflectance are representative for the metallic properties while high melting point, extreme hardness and brittleness, and excellent thermal and chemical stability are related to covalent bonding. These characteristics have been widely exploited for applications in various fields: microelectronic devices, solar cells, electrical interconnections in orthopedic prostheses, cardiac valves and protective and decorative coatings.[1] Recently, titanium nitride has also attracted attention as a promising non-carbon support material for low temperature proton exchange membrane fuel cells.[2] With its high electrical conductivity and resistance to oxidation, TiN has a potential to act as a durable electrocatalyst material.[2–4] Particularly for microelectronics but also other electrocatalytic applications, further deposition of metallic particles or films on top of TiN surface is indispensable. Conventional physical deposition techniques such as physical vapor deposition (PVD) or atomic layer deposition (ALD) have proven efficient in coating titanium nitride with excellent metallic thin films. Unfortunately, these techniques are typically expensive or need a long process time.[5] Electrochemical deposition of different metals on TiN surface has been tackled by numbers of papers as a simple and cost-effective method.[5–9] However, poor adhesion between the deposited metals and titanium nitride still remains a major challenge which is crucial for the development of durable materials.[5] In this case, it should be kept in mind that while these research efforts have only focused on direct electrochemical depositions, another possibility to modify materials surfaces with metallic particles can be realized through different functional groups (amine, sulfonate, carboxylic…) previously grafted on the surface.[10,11] Additionally, these functionalities can serve as nuclei for subsequent electroless depositions of different metals. Metallic thin films on desired surfaces with strong adhesion can be obtained as clearly demonstrated in previous publications.[12–14] More importantly, success in modification of titanium nitride with amino groups would extend the application of this ceramic material towards biosensor development.[15] Hence it is worth underlying the importance of development of efficient organic coating techniques for covalent functionalization of titanium nitride surface.

Among several organic coating technologies available in the literature, the reduction of diazonium cations, developed firstly by Pinson's group,[16] has now been recognized as one of the most powerful tools, since this one-step method provides covalently grafted aryl-layers bearing desired functionalities such as alkyl, nitro, cyanide, carboxylic, ester, alcohol, thiol, and halogenated groups on both conducting and insulating

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surfaces.[17] It is thus interesting to test the versatility of the diazonium chemistry in the case of titanium nitride ceramic. The reduction of diazonium cations can be achieved by different ways such as electrochemical reduction, ultrasonication, photochemistry, microwave heating *etc.*[18] Nevertheless, chemical grafting appears as the simplest method because this technique does not need any supporting equipment (*i.e.* electrochemical power supply, ultraviolet light source, heating or sonicating systems) and works by simply immersing the substrate into the diazonium salt solution with or without the presence of a reducing agent.[19–21] Consequently, chemical grafting will be taken into consideration in this work. First, we will perform spontaneous grafting of TiN with the diazonium salt of 1,4-phenylenediamine. The term "spontaneous" means that the grafting is realized in the absence of any reducing agent. Although the robust efficiency of the grafting through the diazonium route is quite well-accepted, the formation mechanisms as well as the nature of the final bonding between the substrate and aryl-layers are still under discussion in recent publications.[18,21–23] Indeed, we have observed that the spontaneous grafting of arenediazonium salt on germanium surface strongly depends on the oxidation state of the surface itself and working conditions (immersion time, temperature of the solution *etc.*).[21] Small *et al.*[22] demonstrated that the diazonium molecules do not spontaneously form a continuous monolayer on 440C stainless steel immersed in different organic solvents. In particular, it has recently been reported that a thick aminophenylene films of 14 nm can be spontaneously grafted on SU-8 non-conducting substrate in the absence of any reducing agent. In contrary, the thickness of that aminophenylene film prepared with reducing agents is limited to approximately 7–8 nm. Taking into account these observations, it will be interesting to perform chemical grafting of our investigated diazonium salts in the presence of reducing agents. To get more insight into the impact of the assistance of reducing agents, two kinds of reducing agents – iron powder (heterogeneous) and hypophosphorous acid (homogeneous) will be used herein. We also endeavor to discuss as clearly as possible the formation and thickness of the aryl-layers grafted on our TiN substrates through X-ray photoelectron spectroscopy.

Experimental

Chemicals

para-Phenylenediamine ($C_6H_4(NH_2)_2$, ACS reagent 99%), sodium nitrite ($NaNO_2$, ACS reagent ≥97.0%), and hypophosphorous acid solution (H_3PO_2, 50% in water) were obtained from Sigma Aldrich. Iron powder (<10 μm) was obtained from Alfa Aesar. All chemicals were used as received and without further purification.

Sample preparation

Ti/TiN multilayers were deposited by sputtering onto SiO_2/Si substrates (hereafter termed TiN substrate). The sputtering processes were all carried out in a Sigma cluster tool. The Ti/TiN layers were nominally deposited on a substrate maintained at a temperature of 450 °C. The nitriding process was optimized to get multi-layers with thicknesses of 10 nm and 95 nm, respectively for Ti and TiN. Details concerning the preparation of TiN substrates can be found elsewhere.[24] The TiN substrate coupons were cut in 30 mm × 20 mm dimensions and cleaned in 0.5 M hydrochloric acid solution (Fisher) under ultrasonication for 10 minutes. The coupons were covered with vinyl tape while exposing 10 mm × 10 mm area of TiN in the middle of the coupons. Attention was paid to cover Si/SiO_2/Ti/TiN multilayer interfaces completely.

Chemical grafting

The grafting of aminophenyl and carboxyphenyl layers on TiN was carried out at room temperature in open atmosphere. To prepare 2 mM aminophenyldiazonium salt solution, 43 mg of *para*-phenylenediamine was first dissolved in 200 mL of 0.1 M hydrochloric acid solution (pH 1.0), and then 28 mg of sodium nitrite was added, and stirred until a homogeneous solution was obtained. In order to investigate the role of different reducing agents in the grafting process, three sets of samples were prepared. An amount of 50 mL of the solution was then poured in each of the three Pyrex® beakers, and 5 equivalents of one of the two different types of reducing agents – iron powder (28 mg) and hypophosphorous acid (50 μL), was added to the solution. No reducing agent was added to the third beaker to investigate *in situ* spontaneous reduction of diazonium cations by the substrate itself during the grafting process. At this point, TiN substrate coupons were introduced into the three solutions. All experiments were protected from UV light during the grafting. The samples were removed from the solutions after 100 minutes, while no agitation was applied throughout the grafting process. The samples were thoroughly washed with HCl (0.5 M), acetone and ethanol under magnetic stirring, and dried with nitrogen gun.

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) was performed with a monochromatic X-ray photoelectron spectrometer (AXIS Ultra DLD, Kratos Analytical), equipped with micro-focused Al Kα X-ray source (1486.6 eV). Survey scans (in the range of 0 and 1350 eV) and high resolution scans were collected with energy steps of 1 and 0.1 eV, and pass energies of 160 eV and 40 eV, respectively. Charge neutralization gun was used to avoid any surface charge build-up during X-ray scans. Peak fitting procedures were performed using the software CasaXPS (version 2.3.16). The spectral energies were calibrated by setting the binding energy of the C 1s component corresponding to C=C–C bonds to 285 eV.

Results and discussion

Spontaneous grafting of aminophenylene film onto TiN surface from aminobenzenediazonium cations

Although the mechanism of spontaneous grafting is not clear, as mentioned in the introduction, it is well accepted that the grafting through the diazonium chemistry takes place

spontaneously on any conducting substrate which is immersed in the solution containing diazonium cations.[25,26] After 100 minutes of immersion in 0.01 M solution of 4-aminophenyldiazonium cations ($H_2N–C_6H_4–N_2^+$), the treated titanium nitride substrate is characterized by means of XPS and compared to that of the pristine sample. Fig. 1 shows the XPS survey spectra of the bare and modified TiN. While the spectrum of the pristine one presents a typical behavior of TiN substrate with a small peak of unavoidable carbon contamination,[1,27] an increase in the intensity of the C 1s peak clearly indicates the presence of an organic layer on the modified surface.[28]

Indeed, TiN substrate is contaminated by organic materials containing COO (288.3 eV), C–O (286.2 eV) and C–C (284.6 eV) (Fig. 2). With respect to the functionalized surface, the C peak of C–C bonds at 284.6 eV increases significantly as a phenyl layer was grafted on the surface. With the contribution of the C–N bonds of the grafted layer, the intensity of the peak at 286.2 eV also increases. Importantly, a new component centered at 282.6 eV appears after treating TiN substrate in the solution of aminobenzenediazonium cations. Notwithstanding the low intensity, this weak C 1s signal is, however, really important as it was interpreted in the literature as an evidence of the covalent metal–carbon bond between the metal surface and phenyl groups grafted through the diazonium route.[26,28,29] Indeed, bringing out the proof of covalent bonding between the substrates and the grafted layers is still an open subject within the field of organic coating through diazonium chemistry.[26,28,30–33] The C 1s peak found at around 283.0 ± 0.5 eV which corresponds to a carbide carbon was reported to be a direct proof for the existence of a covalent bond between aryl group and different substrates, *e.g.*, iron,[29] nickel,[26] and stainless steel.[28] In the case of TiN, it is important to point out that similarly to the metal–carbon bonds already reported, the corresponding peak in our present work is weak. Nevertheless, we can undoubtedly attribute it to a bond with the diazonium salt, as it was absent in the pristine substrate taken as reference.

As the grafting has been evidenced through the behavior of C 1s core level spectrum, it is necessary to confirm the presence of the expected aminophenyl groups on the surface. We thus analyzed the N 1s core level spectra of the bare and grafted TiN surfaces (Fig. 3). The high resolution N 1s spectrum of the bare TiN can be decomposed into three typical features: one located at 395.9 eV assigned to TiN bonds, one at 397.2 eV assigned to N–O bonds of TiO_xN_y and the last at 399.4 eV assigned to N–H bonds.[1,34] In the case of grafted sample, due to the presence of the organic layer, the intensity of the two peaks TiO_xN_y and TiN is reduced. In contrary, as this coated layer contains certain density of amino functionalities, the peak at 399.4 eV therefore appears with higher intensity as compared with the pristine surface. Besides, an important point to be noted is that the grafting of the aryl layer on TiN can also result from surface-N=N-aryl junctions because the reduction of diazonium may also result in the generation of azophenyl radicals ($H_2N–C_6H_4–N_2^{\bullet}$).[35] The formation of the azo bridges has contributed to evidence the grafting mechanism of aryl layer through the diazonium route.[26,36] The new N 1s peak at 400.4 eV corresponding to the –N=N-linkages obtained with the grafted TiN surface (Fig. 3) is thus in a good agreement with the discussion above.

Similar to the N 1s spectrum, all the characteristics of the TiN materials are observed in the Ti $2p_{3/2}$ spectrum of the bare surface (Fig. 4). This spectrum is best fitted with three components: TiN (TiC) at 455.3 eV, TiO_xN_y at 456.5 and TiO_2 at 458.1 eV.[1,37,38] In line with C 1s and N 1s spectra, the intensity of the Ti 2p peak after grafting is lower than that of the pristine surface due to the presence of the organic layer. Here, another important point to be underlined is that modification of TiN surface leads to a slight variation in the atomic percentage of these

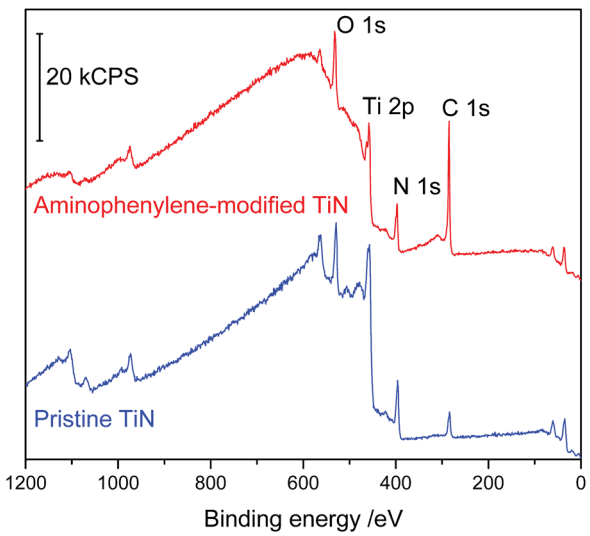

Fig. 1 XPS survey spectra of the bare and modified TiN samples.

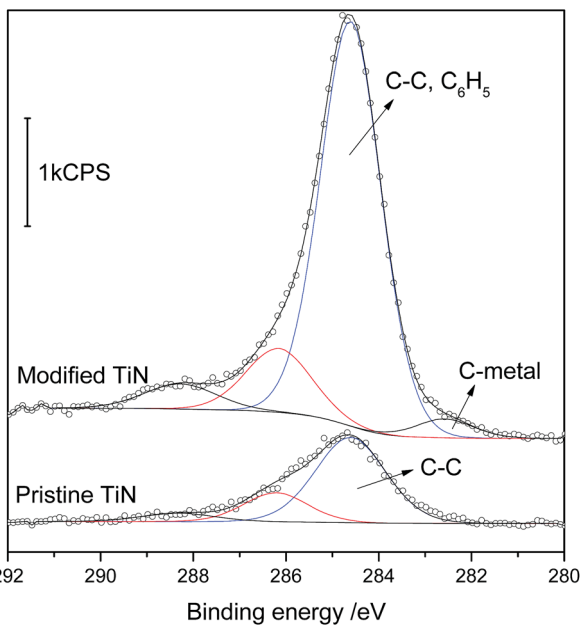

Fig. 2 Decomposed C 1s core level spectra of the bare TiN and the modified samples.

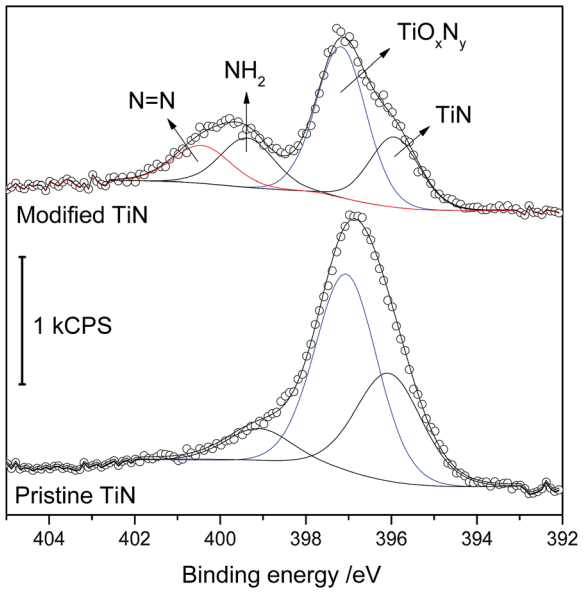

Fig. 3 Decomposed N 1s core level spectra of the bare TiN and the modified samples.

components 43 : 21 : 36 and 40 : 22 : 38 respectively for bare and modified surfaces. Small *et al.*[22] have recently reported that the spontaneous formation of aryldiazonium film on 440C stainless steel affects slightly the percentage of iron bound on the surface. Indeed, our XPS results strongly suggest a covalent functionalization of the aminophenyl groups onto TiN surface by simply immersing the substrate into a diazonium salt solution. Also, it is easy to observe that the aryl layer spontaneously grafted on TiN is quite thin.

The thickness of the aminophenylene grafted layers could be estimated by the standard overlayer model from the attenuation of the Ti 2p peak intensities before and after modification:[39,40]

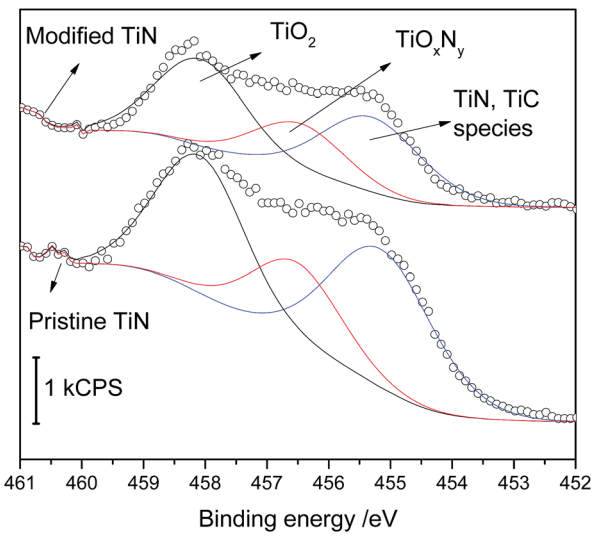

Fig. 4 Decomposed Ti 2p3/2 core level spectra of the bare TiN and the modified samples.

$$I/I_0 = \exp(-d/\lambda \sin \theta) \quad (1)$$

where d is the layer thickness, λ the photoelectron escape depth, θ the takeoff angle, and I/I_0 the ratio of the Ti 2p peak intensities of the bare and grafted surfaces (Fig. 4). In our experiment, the takeoff angle was 90°. With respect to the TiN and TiO_2 materials as well, λ of Ti $2p_{3/2}$ was reported to be in the order of 10–11 Å.[41,42] The thickness of the aminophenylene layer is, at first approximation, found to be 6.4 Å (with a relative error of ~15%). This, in other words, means that the aryl layer spontaneously grafted on TiN surface is close to a monolayer.[43,44] Here, it is worth recalling that both the electrochemical and spontaneous graftings by means of diazonium salts usually provide multi-aryl layers the thickness of which is found to be in the range of few nanometers.[45] A mono aryl layer has been reported mainly in the case of hydrogenated silicon surface completely covered by Si–H groups,[46] and on stainless steel.[22] Competition between native oxide formation and organic film growth at different diazonium salt concentrations was reported as a main reason why diazonium molecules will not spontaneously form a continuous monolayer on 440C stainless steel. Especially for titanium based materials, our very thin layer obtained with TiN also seems to be in line with the work of Griveau's group.[44] Therein, an island-like model was given in order to explain why only mono-aryl layer is obtained with electrochemical reduction of nitrobenzenediazonium tetrafluoroborate onto titanium surface, or more precisely TiO_2 native oxide layer. Since the titanium surface is systematically passivated after air exposure, Griveau and co-workers did not observe any proof of covalent bonding *via* surface carbide in the C 1s core level. They thus postulated that this bond is likely Ti–O–C rather than Ti–C. Actually, metal–O–C bond was already reported by spontaneous grafting of several diazonium salts on copper in its native oxide state.[47] In addition to the proof for covalent bonding through the titanium carbide clearly observed in the C 1s core level spectrum, we believed that metal–O–C bond is another possibility for the grafting of aminophenyl layer on our TiN surface where TiN (TiC), TiO_xN_y and TiO_2 are present. Even though the covalent bonding is quite evidenced in the present work, the grafting of a mono-aryl layer is still questionable. As mentioned in the introduction section, TiN possesses metallic properties and hence it can act as a reducing agent to promote grafting of films from the diazonium ion solutions. Even in the absence of a reducing substrate or added reducing agent, there is slow growth of thin surface films from the diazonium solutions.[23,26] The grafting of aminophenyl layer on TiN in this work can be better discussed through the redox properties of both 4-aminophenyldiazonium cations and the titanium nitride substrate. It was reported that the 4-aminophenyldiazonium cations were reduced at about 0.47 V in HCl medium while the electrochemical oxidation of TiN can start to follow a similar path of an oxidation process at 0.5 V.[37] The spontaneous reaction can therefore proceed *via* an electron transfer from the titanium nitride substrate to the diazonium cation.[26] This, in other words, means that the grafting of aminophenyl layer occurs through the conventional hemolytic dediazoniation mechanism where aryl radical species are produced from that

spontaneous electron transfer.[26] TiN is however different to the other metallic substrates in terms of electrochemical oxidation resistivity. Such characteristic is attributed to the presence of the nitrogen-enriched surface layer of titanium oxynitride with a large electron density that screens the underlying titanium cations and inhibits the oxidation reaction.[37] More importantly, it was also observed that the release of electron from TiN results in a formation and growth of oxide/oxynitride films on the surface of TiN which leads to the retardation (or passivation) of these oxidation processes.[37] Quantification of Ti 2p3/2 spectra equally shows that spontaneous grating onto our titanium nitride surface slightly varies the atomic percentage of TiN, TiO_xN_y and TiO_2: from 43 : 21 : 36 to 40 : 22 : 38 respectively for bare and modified surfaces. That typical behavior of TiN substrate is probably the main reason why the electron transfer is self-limiting after the grafting of only one monolayer on the TiN surface. Additionally, as the spontaneous electron transfer solely happens at TiN species while the surface also contains TiO_2, TiO_xN_y it is believed that the spontaneous grafting does not provide a uniform mono-layer on the entire titanium nitride surface. A similar finding has recently been reported for the case of 440C stainless steel.[22] Further experiments in presence of reducing agents with the object of getting more insight into the grafting of aminophenylene layer on TiN surface may thus be very interesting.

Modification of TiN surfaces with aminophenyl groups in the presence of homogeneous and heterogeneous reducing agents

Fig. 5 presents the XPS survey spectra of the TiN surface modified with aminophenyl functionalities in the presence of hypophosphorous acid and iron powder. As seen here, the behavior of TiN functionalized with aminophenyl groups in the presence of hypophosphorous acid reducing agent is identical to that of the spontaneous grafted TiN; *i.e.*, the grafted aryl layer is thin. We still observe clearly all the main elements of the TiN substrate. In contrary, the grafted aryl layer obtained with iron powder is quite thick. Ti 2p almost disappears in its XPS survey spectrum (S1, in ESI†). Indeed, the C 1s core level spectrum in the case of using hypophosphorous acid is quite similar to the one obtained without reducing agent (not shown here). Also, a weak peak of titanium carbide at 282.6 eV is required to best fit the C 1s spectrum. In the case of iron powder, the C 1s spectrum behaves as a thick aminophenylene film as already observed for the stainless steel surface in a previous work.[39]

In line with the C 1s core level spectrum, the appearance of a new N 1s peak at 400.4 eV representing the diazo bridges as well as the significant increase in the intensity of the amine peak at 399.4 eV (Fig. 6) allows us to confirm the grafting of the aminophenyl functionalities on the surface of titanium nitride substrates in the presence of both homogeneous and heterogeneous reducing agents. Similar to the spontaneous grafting, the aminophenylene grafted in the presence of reducing agents does not incorporate any amount of diazonium ion which is characterized by the N 1s peaks at 403.8 and 405.1 eV. The N 1s peaks of TiO_xN_y and TiN of the TiN backbone are still observed

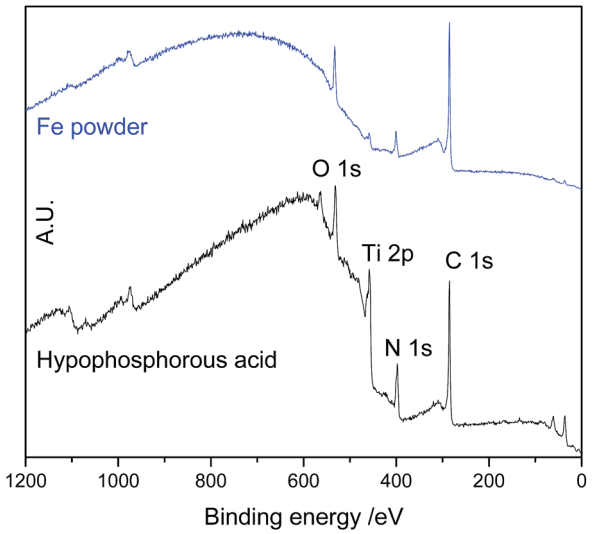

Fig. 5 XPS survey spectra of the aminophenylene-TiN surfaces grafted in presence of hypophosphorous and iron powder.

in both cases. These peaks are more intense in the case of homogeneous reducing agent. This, however, can be explained easily by noting the fact that the two aryl layers obtained with hypophosphorous acid and iron powder differ in terms of thickness.

Indeed, by using the standard overlayer method described above, the thicknesses of these aryl layers are estimated to be 7.1 and 60.0 Å, for the cases of using hypophosphorous acid and iron powder, respectively. Let us insist next on the grafting mechanism of the aminophenylene layers onto TiN with presence of these two kinds of reducing agent. It is remarkable that we equally obtain a near mono-aryl layer in the presence of hypophosphorous acid. The observed behavior is completely

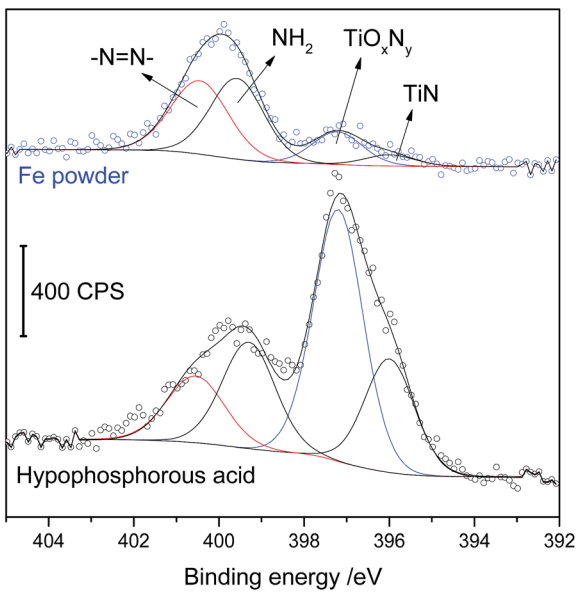

Fig. 6 N 1s core level spectra of the aminophenylene-TiN surfaces grafted in presence of hypophosphorous and iron powder.

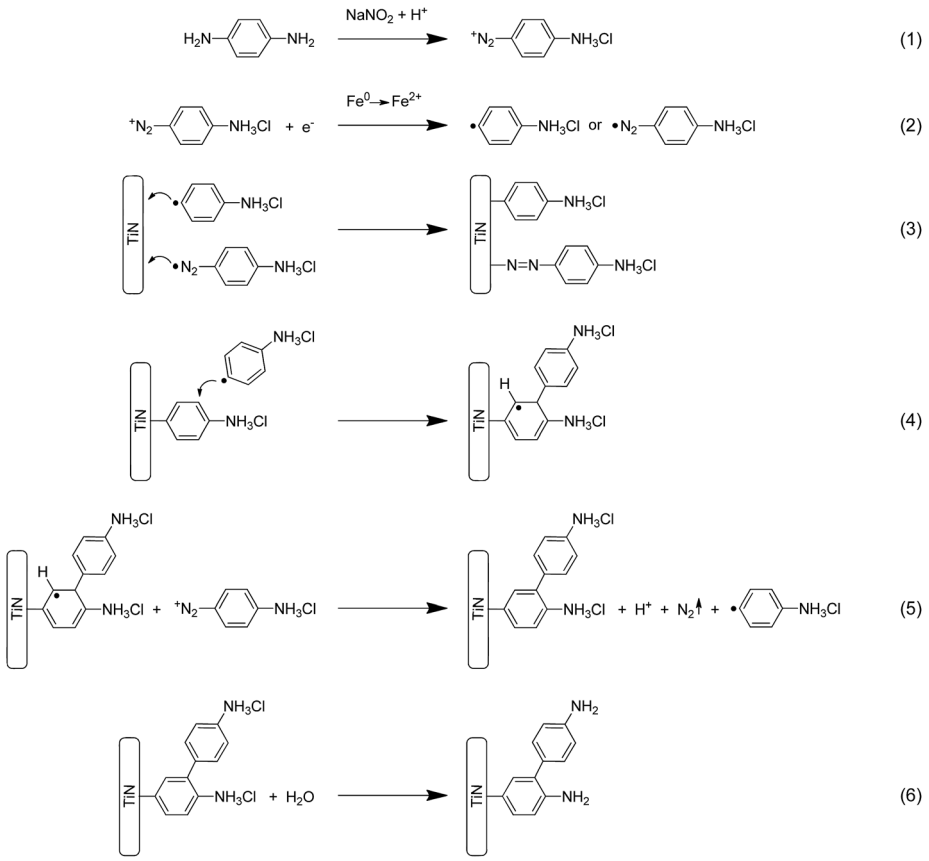

Fig. 7 The mechanism of grafting of polyaminophenyl layer on the surface of titanium nitride.

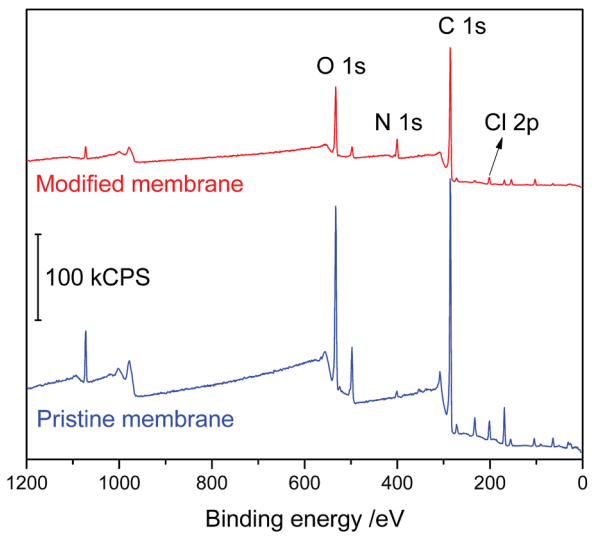

Fig. 8 XPS survey spectra of the bare and modified Selemion CMV membrane.

different as compared with the grafting of aminophenylene on SU-8 insulating substrates, recently published by Downard *et al.*[23] In our special case, the obtained result is however explainable as follows: we added an excess amount of hypophosphorous reducing agent (5 times higher than that of the diazonium cations). It is thus believed that all diazonium cations were rapidly converted to aminophenyl radicals in the solution. When we immerse the TiN substrates in the solution which contains only the aminophenyl radicals, the radicals near the substrates immediately react with the surface to form a very thin layer. According to the hemolytic dediazoniation of diazonium salt mechanism proposed by Pinson and co-workers,[46] and recently developed by other groups,[23,26] the growth of thick film requires the involvement of the diazonium cations. Under our working condition, it is reasonable to assume that no diazonium cations remain after adding an excess amount of homogeneous reducing agent into the solution, and hence the film growth does not take place.

In the case of iron powder heterogeneous reducing agent, our patented "Diazonium Induced Anchoring Process" (licensed GraftFast™ process) can be given here to describe the whole grafting process.[19,20] The mechanism to graft a polyaminophenyl layer on the titanium nitride surface involved diazotisation of the *p*-phenylenediamine in acidic solution (Fig. 7-1). When iron powder was added into the solution, reduction of the aminophenyldiazonium cations ($H_2N–C_6H_4–N_2^+$) generates the aminophenyl radicals ($H_2N–C_6H_4^{\bullet}$) or azophenyl radicals ($H_2N–C_6H_4–N_2^{\bullet}$) (Fig. 7-2). These radicals immediately graft onto TiN to form the first mono-aryl layer (Fig. 7-3). The growth of mixed layers involving phenyl radicals (or azophenyl ones) takes place according to reactions (Fig. 7-4 and 5). Rinsing

the obtained grafted TiN surface by DI water leads to the deprotonation of NH_3Cl groups and provide us with aminophenyl functionalities (Fig. 7-6). It should be kept in mind that even though we added five equivalents of iron particles in the solution only a small fraction of iron atoms at the surface of the iron particles participated in the reduction reaction of the diazonium cations surrounding the particles. The radicals are generated as a function of time in the presence of iron powder in the solution containing diazonium cations. Besides, it should be noted that iron powder can also reduce protons in the solution. This reaction leads to the generation of hydronium radicals which, in turn, can be involved into the growth of the aryl layer onto the TiN substrates as already discussed elsewhere.[48] Additionally, by the gravitational force, all iron particles were found to be at the bottom of the experimental beakers. The radicals, which play an important role in the growth of the aryl film, are generated at the bottom of the working beakers. In order for these radicals to be able to participate to the formation of aryl layer on the solid substrates immersed in the solution, the mass transfer including diffusion and convective conditions must equally be taken into account. In general, under our working conditions, a multi-aryl layer structure is usually obtained on any substrate in acidic solution containing of 4-aminophenyldiazonium cations with iron powder. In the present work, a multi-aminophenylene layer of 6 nm has been grafted onto the TiN substrate.

Next, we make a comparison between the thickness of aminophenylene film on TiN and that obtained with another kind of substrate (Selemion CMV cation exchange membrane) under identical working conditions: using iron powder as reducing agent, strongly acidic solution (HCl), immersion time, steady state (without agitation), room temperature, open air. Selemion CMV membrane is prepared from a blend of polyvinyl chloride (PVC) and a copolymer synthesized from styrene and divinylbenzene. The copolymer is then functionalized by the introduction of a sulfonate ion exchange group.[20] Thanks to the ion exchange property, the membrane is also a conducting material but unlike titanium nitride, it does not behave metallically. Fig. 8 shows XPS survey spectra of the membrane surface before and after modification. The bare CMV membrane spectrum exhibits peaks at 1072 eV (Na 1s), 977 eV (O KLL Auger peak), 532 eV (O 1s), 497 eV (Na KLL Auger peak), 228 eV (S 2s), and 169 eV (S 2p) characteristic of the sulfonate groups together with those at 271 eV (Cl 2s) and 200 eV (Cl 2p) attributed to the PVC backbone. These typical peaks of the pristine membrane are still observed after treatment in diazonium solution. Complete XPS characterization in order to confirm the grafting of aminophenyl groups onto the membrane surface was discussed in detail in our previous work.[20] The present work will only focus on the thickness of the grafted aryl layer. The attenuation of the Cl 2p peak intensities of the PVC backbone from before to after modification is accounted for estimation of the modified layer's thickness. For the Cl (2p), the photoelectron escape depth equals to 14 Å.[49] The Cl 2p core level spectrum for the unmodified CMV membrane is characterized by the $2p_{3/2}$ (200.6 eV) and $2p_{1/2}$ (202.2 eV) doublet with the expected 2 : 1 ratio of the peak intensities (S2, in ESI†). A similar spectrum was also obtained with the modified membrane, but the intensity of the peaks decreased considerably. From the intensity of these peaks before and after modification, the thickness of the grafted aminophenylene layer is estimated to be 1.5 nm which is 4 times thinner in comparison with that grafted on TiN surface. Under our working conditions, the CMV membrane exclusively differs from the titanium substrates in term of the metallic properties. Aside from TiN and CMV membrane in this work, a thick aminophenylene film (9.8 ± 1.5 nm) has been reported to graft onto stainless steel surface.[39] Our obtained results clearly show the important role of the conductivity of the surface, which can itself act as a reducing substrate in the diazonium solutions towards the formation of thick multi-aryl layer.

Conclusions

Recent efforts have concentrated on using reduction of diazonium salts, a well-established technique in the field of surface coating and technologies towards various materials at the laboratory scale, to functionalize the real industrial materials such as stainless steel,[22] SU-8 non-conducting photoresists[23] as well as titanium nitride in the present paper. The hemolytic dediazoniation mechanism fits well the grafting of aminophenyl layers onto titanium surface even though spontaneous grafting or grafting in presence of hypophosphorous acid as reducing agent, provides TiN surface with only near monophenylene layer. The observed behavior is understood by noting that the resistance against electrochemical oxidation of the TiN materials self-limits the spontaneous grafting at very thin layer while a complete conversion of diazonium cations to the aryl radicals due to the addition of an extra amount of hypophosphorous reducing agent into the working solution does not allow the growth of multi-aryl layers on TiN surface. In the case of grafting onto TiN in the presence of iron powder, in combination with the thickness of aminophenylene layers previously grafted on polymeric ion exchange membrane and stainless steel, our result however leaves open fundamental questions about the contribution of the electrical properties of the substrates with respect to the formation of aminophenylene film. These points need further investigations accounting a wide range of working conditions in order to contribute to a better understanding of the diazonium chemistry. Notwithstanding those facts, this work clearly demonstrates that diazonium chemistry could be a promising method for covalent grafting of different functionalities onto titanium nitride surface. Furthermore, the process simply works by immersion of these durable substrates in solutions containing the dissolved diazonium salts. As clearly indicated in the introduction, these functionalities grafted on TiN through diazonium chemistry can serve for subsequent electroless deposition of various metals (nickel, copper…) on titanium nitride. The covalently attached organic layer through diazonium chemistry is anticipated to provide strong adhesion and uniform coverage of metallic thin films on the surface of titanium nitride, and therefore may be explored as an alternate approach to the direct electrochemical deposition method, in order to metallize the surface of titanium nitride.

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